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# 效应物对蘑菇酪氨酸酶的抑制作用及其抑制机理的研究

Studies on the inhibitory effects and inhibitory mechanisms  
of inhibitors on the activity of Mushroom Tyrosinase

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## 摘 要

酪氨酸酶 (EC. 1. 14. 18. 1) 是一种含铜的氧化还原酶, 广泛存在于微生物、动植物以及人体内, 能将酪氨酸转化成多巴醌, 进而形成黑色素; 过量的黑色素形成能产生色素沉着性疾病以及能使果蔬褐变, 因此, 研究酪氨酸酶抑制剂具有十分重要的意义。

本论文以蘑菇酪氨酸酶为研究对象, 筛选抑制剂并研究其抑制机理, 并总结了抑制剂的构效关系, 同时探讨了化妆品中的一些化合物对酪氨酸酶的抑制作用, 研究结果和内容如下:

分别研究了对羟基苯甲酸酯类化合物对羟基苯甲酸甲酯、乙酯、丙酯、丁酯; 水杨酸甲酯、水杨酸乙酯以及水杨酸衍生物 3, 5-二硝基水杨酸、5-磺基水杨酸; 邻苯二胺、对苯二胺对酪氨酸酶的抑制作用, 这些化合物对酪氨酸酶具有不同程度的抑制作用, 磺基水杨酸和邻苯二胺对酪氨酸酶具有激活作用。

分别研究了苯二甲酸类化合物邻苯二甲酸、间苯二甲酸、对苯二甲酸对酪氨酸酶的抑制作用, 研究表明邻苯二甲酸对酪氨酸酶没有抑制作用, 间苯二甲酸对酪氨酸酶具有较弱的抑制作用, 而对苯二甲酸对酪氨酸酶具有较强的抑制作用, 对苯二甲酸对酪氨酸酶的抑制为混合型抑制。

分别研究了苯乙醛、苯乙酸、苯乙醇; 呋喃化合物糠醛、糠酸、糠醇、1, 4-丁内酯、顺丁烯二酸酐; 萘环化合物 1-萘酚、2-萘酚、1-萘乙酸; 脂肪酸化合物正辛酸、山梨酸、正己酸、巴豆酸、正丁酸对酪氨酸酶的抑制作用, 这些化合物对酪氨酸酶具有不同程度的抑制作用, 研究了这些化合物对酪氨酸酶的抑制机理, 研究表明这些化合物对酪氨酸酶均为可逆抑制, 测定了这些化合物对酪氨酸酶的抑制常数, 同时研究了这些化合物对酪氨酸酶单酚酶活力的影响, 结果表明, 这些化合物对酪氨酸酶单酚酶活力具有一定的抑制作用, 苯乙醛对酪氨酸酶单酚酶没有抑制作用。

合成了呋喃丙烯酸、2-氯苯丙烯酸、2, 4-二氯苯丙烯酸、3, 5-二甲氧基苯丙烯酸, 研究了这些化合物对酪氨酸酶的抑制作用, 研究表明这些化合物对酪氨酸酶具有较强的抑制作用, 其对酪氨酸酶的抑制为可逆抑制, 抑制类型均为反竞争抑制; 同时研究这些化合物对酪氨酸酶单酚酶活力的影响, 结果表明, 这些化合物对酪氨酸酶单酚酶活力具有一定的抑制作用。

合成了乙酰水杨酸、乙酰对羟基苯甲酸，研究了这些化合物对酪氨酸酶的抑制作用，研究表明这些化合物对酪氨酸酶具有较强的抑制作用，它们对酪氨酸酶的抑制为可逆抑制，乙酰对羟基苯甲酸对酶的抑制类型为混合型抑制。

研究了化妆品中的化合物保湿剂：乙二醇、丙二醇、丙三醇、肌醇、甘露醇；防腐剂苯甲醇、对羟基苯甲酸；果酸类化合物：甘醇酸、乳酸、苹果酸、酒石酸、柠檬酸、二苯乙醇酸对酪氨酸酶活性的影响情况，研究表明保湿剂类化合物对酪氨酸酶没有抑制作用，防腐剂化合物对酪氨酸酶具有一定的抑制作用，苯甲醇和对羟基苯甲酸对酪氨酸酶的抑制均为可逆抑制，抑制类型为分别混合型和竞争型，果酸类化合物对酪氨酸酶抑制作用最强的为甘醇酸，甘醇酸对酪氨酸酶的抑制为混合型抑制，其它果酸类化合物对酪氨酸酶具有较弱的抑制作用。

通过本课题的研究，为高效酪氨酸酶抑制剂的开发以及化妆品上的应用奠定了基础。

**关键词：**酪氨酸酶，抑制剂，抑制机理，抑制类型，二酚酶，单酚酶

## Abstract

Tyrosinase (EC. 1. 14. 18. 1), a copper-containing redoxidase enzyme, is widely distributed in microorganisms, animals, plants and human beings. It is responsible for transforming of L-tyrosine to DOPAquinine, which can produce melanin in a series steps. The abnormal formation of melanin may bring out serious diseases in human beings and browning in fruits and vegetables, so, it's of great interest to inhibit the activity of tyrosinase.

Screening the mushroom tyrosinase inhibitors and studying their inhibitory mechanism have been conducted. In view of the relationship between inhibition activity and structure of tyrosinase inhibitors, at the same time, inhibition effects of tyrosinase by the compounds in cosmetics also have been studied. The contents and results are as follows:

The effects of 4-hydroxybenzoic acid methyl ester, 4-hydroxybenzoic acid ethyl ester, 4-hydroxybenzoic acid propyl ester, 4-hydroxybenzoic acid butyl ester, salicylic acid methyl ester, salicylic acid ethyl ester, 3, 5-dinitrosalicylic acid, 6-sulfosalicylic acid, o-phenylene diamine and p-phenylene diamine on tyrosinase were studied, most of them can inhibit the activity of tyrosinase more or less, but 6-sulfosalicylic acid and o-phenylene diamine can activate the tyrosinase activity.

The inhibition effects of phthalic acid, isophthalic acid and terephthalic acid on mushroom tyrosinase also have been investigated, results showed that phthalic acid had no inhibition effect on tyrosinase activity, isophthalic acid had a weaker inhibition effect than terephthalic acid, the inhibition mechanism of terephthalic acid is reversible, and its inhibition type is mixed.

The inhibition effects of 2-phenylacetaldehyde, 2-phenylacetic acid, 2-phenylethanol, furfural, furoic acid, 2-furylcarbinol, 1, 4-butyrolactone, maleic anhydride, 1-naphthol, 2-naphthol, rhodofix, n-octanoic acid, sorbic acid, n-hexylic acid, crotonic acid and ethyl acetic acid on mushroom tyrosinase have been determined, these compounds all have inhibition effects on tyrosinase activity, and the inhibition mechanism were reversible, the inhibition constants have been determined,

the inhibition effects on monophenolase have been studied as well, results indicate that almost all of the compounds have inhibition effects on monophenolase except 2-phenylacetaldehyde.

Synthesis of furan acrylic acid , 2-chlorocinnamic acid, 2,4-dichlorocinnamic acid, 3,5-dimethoxycinnamic acid, and studying the inhibition effects of these compounds on the activity of both monophenolase and diphenolase, all of them can inhibit the activity of both monophenolase and diphenolase, and the inhibition mechanisms are reversible, the inhibition type are noncompetitive.

Synthesis of acetylsalicylic acid and acetyl-4-hydroxybenzoic acid, and studying the inhibition effects of these compounds on the activity of diphenolase, they can inhibit the activity of tyrosinase, and the inhibition mechanisms are reversible, the inhibition type of acetyl-4-hydroxybenzoic acid is mixed type.

The inhibition effects of some compounds in cosmetics have been researched, humectants: 2-ethanediol, propanediol, glycerol, mannitol, sorbitol, inositol; fruit acids: glycolate, lactate, malate, tartrate, citrate, the compounds of humectants nearly have no inhibition effects on the activity of tyrosinase, but fruit acids glycolate has strong inhibition effect, the other fruit acids have weak inhibition effects, the inhibition mechanism of glycolate is reversible, and its inhibition type is mixed.

The synthesis and inhibitory mechanism of new potential tyrosinase inhibitors were done in the study, which provided a foundation to develop high effective inhibitors and application in cosmetics.

**Key words:** Tyrosinase, inhibitor, inhibition mechanism inhibition type monophenolase, diphenolase



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